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NUCLEATION IN DENSE FLUIDS OF HARD SPHERICAL COLLOIDS

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The transformation of a supercooled fluid to the crystal phase remains one of the more interesting aspects of condensed matter. Detailed experimental studies of the mechanisms by which the new phase nucleates and grows in atomic or molecular fluids are impeded by very fast growth rates, the liberation of latent heat and the domination of heterogeneous nucleation on impurities and container walls[1]. These difficulties are generally absent in colloidal suspensions because, firstly, the slow diffusive particle motions result in easily accessible crystallization rates, secondly, the particle numbers per volume are typically so small that the magnitudes of the (excess) thermodynamic properties, including latent heat, are negligible and, thirdly, typical sample sizes are so small (relative the particle size) that heterogeneous nucleation is avoided[2].

In this lecture we describe the crystallization of suspensions of (nearly) identical polymer spheres, stabilized by thin macromolecular coatings that produce short-ranged repulsive interparticle forces. The similarity of the disorder-order transition, observed in these systems, to the freezing-melting transition expected for the perfect hard-sphere system suggests that the interactions among the polymer particles can be regarded as hard-sphere-like[2].

The particles used in this work consist of poly-methyl methacrylate (PMMA) cores of radius R ($\cong$200nm) sterically stabilized by thin (~10nm) layers of poly-12-hydroxystearic acid (PHSA). Suspending these particles in a controlled mixture of decalin and carbon disulphide provides concentrated suspensions of sufficiently low turbidity that the effects of multiple light scattering are negligible.

Freezing, melting and glass transition volume fractions in these suspensions[2,3], respectively at ϕ_f=0.494, $\phi_m \approx 0.545$ and $\phi_g \approx 0.58$, are in accord with computer simulation results for hard spheres. Below ϕ_g crystallization appears to occur through the homogeneous nucleation and growth of randomly oriented crystals, distributed randomly throughout the sample volume[4].

In the spectrometer used for the measurements the number of crystals in the scattering volume ($\approx$1 cm^3), at least for high sample concentrations ($\phi \geq \phi_m$), is sufficiently large to obtain a reasonable estimate of the orientationally averaged diffraction pattern despite the fact that the detector intercepts the Debye-Scherrer cone in a plane. The orientationally-averaged diffraction pattern consists, in part, of a sharp Bragg reflection from close-packed layers of particles superimposed on a broad diffuse background associated with the random stacking of these layers[5]. The detector is positioned to bracket the main Bragg peak with a resolution (in reciprocal space) significantly larger than the inverse linear dimension of the largest crystals observed.

After tumbling a given sample, to shear melt any crystals, it was placed in the spectrometer and measurement of the intensity commenced (at t=0) and continued at preset time intervals up to t_f=20 hours. We obtain the time-resolved Bragg peak after correcting the raw data for the single particle form factor and the (time-dependent) effect of the fluid[6]. From the area under the resulting peak,

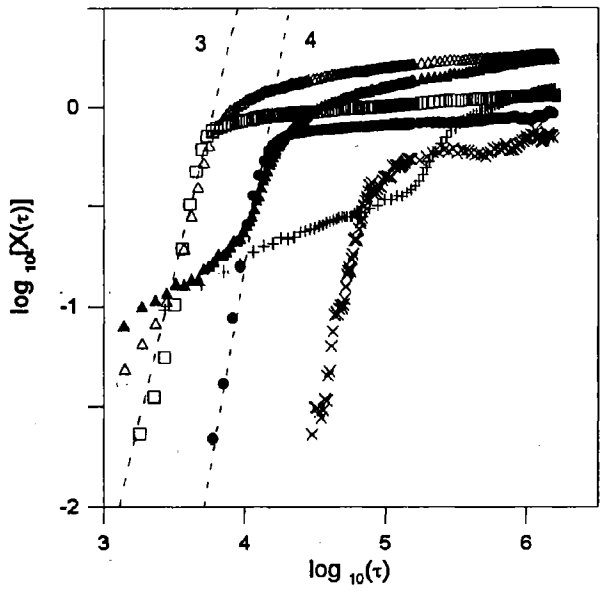

Fig. 1. Crystal fractions, $X(\tau)$, versus time, τ, for sample volume fractions ϕ=0.530 (×), ϕ=0.537 (●), ϕ=0.548 (□), ϕ=0.557 (Δ), ϕ=0.565 (▲), and ϕ=0.575 (+). Time is expressed in units of the free particle Brownian time. Power laws, τ^{δ} (dashed lines), are indicated by their exponents δ.

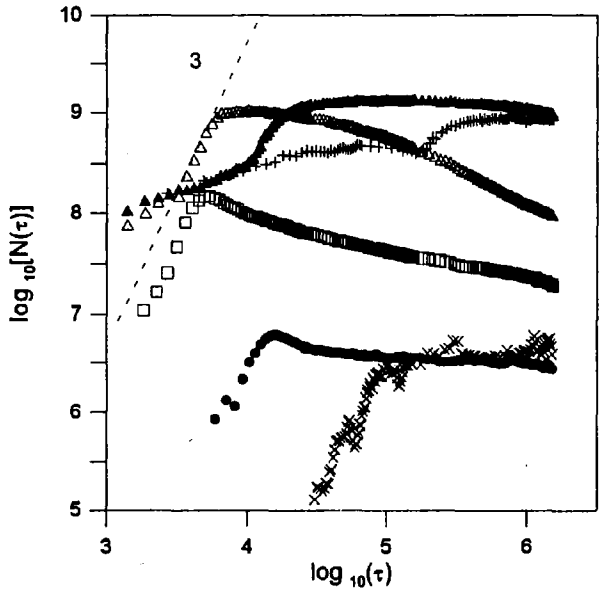

Fig. 2. Number of crystals versus time. Sample concentrations as indicated in Fig. 1.

its width at half its maximum and its position, we obtain the amount (or fraction) of crystal, X(t), the average linear crystal dimension, L(t), and, assuming the close-packed structure, the crystal volume fraction, $\phi_c(t)$. The number of crystals is then calculated from, $N(t)=X(t)/L^3(t)$.

Fig. 1 shows that stages of rapid fluid to crystal conversion, $X(\tau)\sim\tau^4$ for $\phi\lesssim\phi_m$ and $X(\tau)\sim\tau^3$ for

$\phi_m \lesssim \phi \lesssim \phi_g$, cross over to stages of much slower conversion, $X(\tau) \sim \tau^{\nu}$, $\nu \lesssim 0.1$. As ϕ approaches ϕ_g a gradually slower (sublinear) conversion regime precedes the rapid conversion stage. A qualitative change in crystallization kinetics is evident from the time dependence of the number of crystals, $N(\tau)$ shown in Fig. 2. This indicates that the number as well as the maximum rate of crystal addition increase rather suddenly, by more than a hundred fold, as the melting concentration is traversed. Note, in particular, that at higher concentrations fluid to crystal conversion seems to be dominated by rapid, accelerated (ie $N(\tau) \sim \tau^{\mu}$, $\mu > 3$), addition of crystals to number densities so large that significant crystal growth is precluded.

The initial slow (sublinear) rates of crystal addition (Fig. 2) and conversion (Fig. 1), most apparent at the highest concentrations, are probably due to relaxation of the sheared (tumbled) fluid. At long times the slow increase in L and the accompanying decrease in N, while X is almost constant, suggest coarsening; the growth of the larger crystals at the cost of the smaller ones.

Mechanical equilibrium between the growing crystals and the surrounding fluid requires that the particle concentration in the crystals is greater than that of the fluid. Fig. 3, which shows the crystal volume fraction $\phi_c(\tau)$, inferred from the position of the Bragg peak, indicates that this is indeed the case. For $\phi = 0.537$ (ie $< \phi_m$) $\phi_c(\tau \approx 0) \approx 0.57$; this value exceeds ϕ_m. It is gratifying that at the conclusion of the measurement ($t = t_f = 20$ hours) approximate equilibrium has been established since $\phi_c(t_f) = 0.55 \approx \phi_m$. For $\phi = 0.565$ we see that $\phi_c(\tau \approx 0) = 0.625$ but that the system, after being left undisturbed and allowed to crystallize for 20 hours, is still some distance from equilibrium is indicated by the fact that $\phi_c(t_f) \approx 0.58$, significantly above the initial concentration of the metastable fluid.

In fact, according to the equations of state for the hard sphere crystal and (metastable) fluid the first crystals, identified in deeply quenched fluids, are in pressure balance with the initial (sheared) colloidal fluid[6]. Fig. 3 also indicates that the volume fraction, $\phi_c(\tau)$, of the crystal phase decreases with time and that the time interval of the strongest rate of fluid to crystal conversion (Fig. 1) coincides with that of the most rapid decrease in ϕ_c.

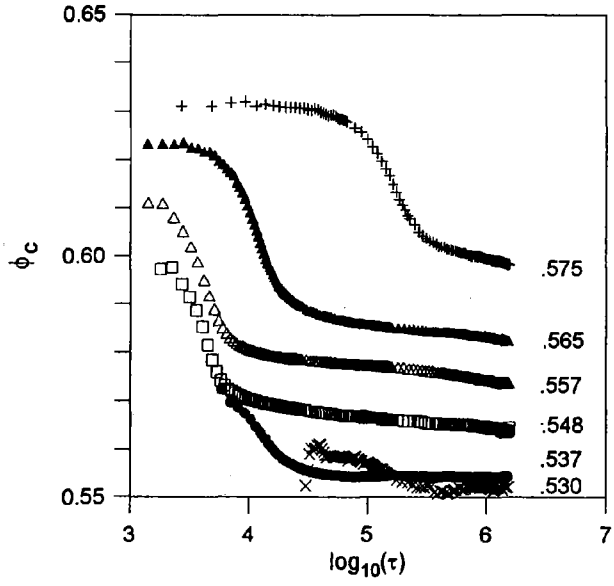

Fig. 3. Particle concentration of the crystal phase, $\phi_c(\tau)$. Sample concentrations as indicated in Fig. 1

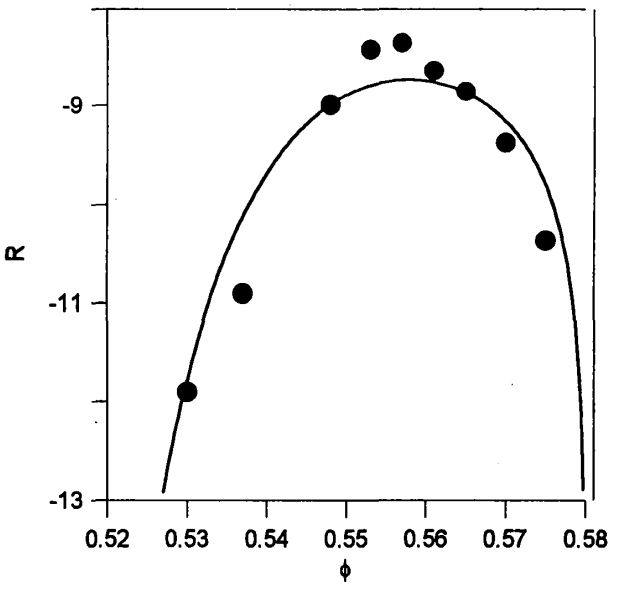

Fig. 4. Experimental maximum nucleation rate densities (dots) and best fit to classical theory (line), as a function of sample concentration.

Finally, with the aid of Fig. 4, which compares the maximum rates of nucleation calculated from Fig. 2 with results from classical nucleation theory[7], the accelerated rates of nucleation seen in Fig. 2 can be interpreted as follows. When a suspension is (density) quenched (by preparation and tumbling) to a concentration that exceeds the value ($\approx\phi_m$) where the nucleation rate density has a maximum the initial conversion, occurs through nucleation of crystals that are compact (Fig. 3) relative to the metastable fluid. The resulting drop in the average density of the remaining fluid has two consequences: First, the nucleation rate increases and, second, the lattice spacing of the crystals increases due to the drop in pressure of the fluid that surrounds them.

We draw the following conclusions. In order to maintain mechanical equilibrium, the first identifiable crystals formed in a concentrated metastable fluid suspension of hard spherical polymer particles have a significantly higher density than the fluid. As a result the density of the fluid and the pressure it exerts on the crystals decrease causing the average crystal lattice spacing to increase. In deeply quenched fluids, the drop in density also causes the nucleation rate to accelerate.□

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